

# Pesticide fate in soil-sediment-water environment in relation to contamination preventing actions

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## Abstract

The increasing use of pesticides during the past five decades has highlighted the potential risk posed by pesticides to the environment. The unequivocal presence of pesticide residues in soil, sediment and water samples has raised public and scientific awareness. Pesticides are exposed to environmental conditions and thus they can be degraded by the influence of physical, chemical and biological factors, volatilized, adsorbed by soil colloids and transported offsite by surface runoff and leaching. The quantity of each pesticide that can be found in soil, sediment and water bodies depends on the significance of all the afore-mentioned processes. Moreover, agricultural practices followed during and after pesticide application also influence the environmental dispersion of pesticides. Climate change, new technologies used in pesticide formulation (nanopesticides, resolved isomers), and new application-release strategies are expected to determine the fate of pesticide in the soil-sediment-water environment.

## Addresses

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## Keywords

Nanopesticides, Adsorption, Leaching, Degradation, Runoff, Preferential flow.

## Introduction

There are several routes through which pesticides can contaminate the environment. Point-source or diffuse contamination and pesticide dispersion to different environmental compartments is affected by several processes. Pesticides are deliberately or unintentionally released to nearly all biospheres. There is evidence that soils, sediments, surface- and ground-water bodies of agro-ecosystems are contaminated with variable levels of pesticide residues (ppt – ppm range) [1]. Pesticide

transport and degradation (dissipation) are the two main routes/causes that affect pesticide toxicity and efficacy. Pesticide transfer includes volatilization, spray drift, wash and runoff, leaching, and lateral drainage, whilst pesticide degradation encompasses photolysis, biotic and abiotic breakdown. Environmental contamination by pesticides may also occur via dust generated during the sowing of coated/dressed seeds [2,3\*\*]. Moreover, pesticide residues that remain in plant material can be released into the soil during litter breakdown [4]. Monitoring and modeling studies have been used to explore the fate of pesticides in soil-sediment-water. Results from numerous monitoring studies have been used to calibrate and validate pesticide fate models and eliminate uncertainties [5]. In this article, the issue being discussed involves what is currently known about the factors affecting pesticide fate and distribution in soil, sediment, surface- and ground-water bodies through the prism of contamination preventing actions.

## Soil and sediment

Soil and sediments are the major deposits of pesticides (as these chemicals mostly settle there) affecting the overall dispersion of pesticides to other environmental compartments. The mobility as well as persistence of pesticides is controlled by their adsorption into soil. Organic matter and clay content/composition, soil minerals, soil pH and temperature play an important role in pesticide adsorption into the soil [6]. Pesticide immobilization and sequestration as nonextractable/bound residues is generally considered to be based on various physico-chemical properties involving interactions between pesticides and soil organic matter or clay [7]. The formation of bound residues in soil generally decreases the leaching, runoff, uptake, action, and bioavailability of pesticides [8]. Nonetheless, under certain conditions, bound residues can be released to aqueous or gaseous phases.

Plant uptake processes together with adsorption into soil compartments, chemical or photochemical degradation, biodegradation, leaching and runoff cause a rapid decrease of pesticide concentrations in soil water. Nevertheless, pesticides can remain in measurable concentrations in the soil for years [9]. Vryzas et al. [10\*\*] analyzed concentrations of alachlor and metolachlor in soil water and have reported their long persistence. Alachlor and metolachlor were detected 39 and 18 months after their application (0.53 µg/L and 10 µg/L), respectively. These observations are in line with those of other studies which have shown that pesticides with low DT<sub>50</sub> values (few days), characterized as non-

persistent, can be detected at low concentration (ppt–ppb) many months after their application. In other cases, pesticides with DT<sub>50</sub> values higher than 6 months (i.e., imidacloprid), have been found to accumulate in soil after consecutive annual applications [11].

Dissipation of pesticides in soil may occur by several ways including leaching, drainage, biotic and abiotic degradation, evaporation, dilution, plant uptake and runoff. Dissipation of pesticides in soils depends on several factors, such as soil texture, organic matter content, cation exchange capacity, pH, soil water content, distribution of the porosity, macroporosity, ultra-violet radiation, air temperature, microbial community structure and its ability to degrade pesticide residues, which all can vary from place to place [8]. Soil temperature also affects the sorption and degradation process of pesticides [7]. It has been estimated that half-lives of pesticides in soil range over one order of magnitude under various conditions (soil depth, region, season, etc) [12]. Soil moisture affects sorption, leaching and degradation of pesticides within the soil profile. In dry soil conditions pesticide adsorption is greater and microbial activity is reduced. Acetamiprid half-life was 10 times greater under dry conditions compared with field water capacity [9]. On the other hand, pesticide dissipation studies have shown that half-lives of many pesticides are dose-dependent [13]. Although the abiotic processes contribute to the degradation of specific pesticides, biodegradation is the most studied dissipation process. Microbial community structure and activity play a primary role in the degradation of pesticides. Enhanced biodegradation has been reported for many pesticide classes after their repeated application [14,15\*]. Enantioselective behavior of chiral pesticides under different soil amended treatments has been recently observed [16\*].

Leaching of pesticides through the soil profile is responsible for the contamination of groundwater. The extent of leaching is highly dependent on soil properties, pesticide physicochemical properties, formulation types, distribution of rainfall events or irrigation strategy and hydrogeological processes [17]. Commercial formulation of pesticides might have different leaching potential compared to its pure active ingredient. The presence of surfactants, emulsifiers, solvents, and other adjuvants in commercially-available formulations may affect the leaching and dissipation process of pesticides [18,19]. Several authors reported on the effects of soil amendment (sewage sludge, charcoal, manure, olive-mill waste and biochar) and nutrients on pesticide leaching [20–23\*,24]. The introduction of nanotechnology in pesticide formulation (nanopesticides) may modify the environmental fate of active ingredients since the objective of many nanoformulations is to achieve the controlled/slow release of active ingredient or to protect it from rapid degradation and off-

target transport. Enhanced photostability, reduced volatilization, and slower release are among the processes reported to be affected by nanoformulation of pesticides [25–28\*\*]. However, in other cases nanoformulation may facilitate the transport of active ingredients within the soil profile [29]. Recently, it has been reported that the sorption and degradation of bifenthrin nanoformulation differed by a factor of 10 and 1.8, respectively, compared to the pure active ingredient and the conventional formulation [30\*\*]. Moreover, the leaching potential of nanopesticides is remarkably different between various soil types compared to the conventional formulations [28\*\*,30\*\*–32].

Sediments and suspended materials play an important role in the environmental fate of pesticides in surface water bodies. Physical, chemical, and biological processes in the water-sediment environment determine the spatial and temporal distribution of pesticide concentration in surface water. Banned organochlorine pesticides are still detected in sediment samples decades after their last use [33–36]. Sorption of hydrophobic pesticides has been studied extensively and their sediment-water distribution can be easily predicted through empirical relationships, such as soil organic carbon-water (K<sub>oc</sub>) and octanol–water (K<sub>ow</sub>) partition coefficients. On the other hand, relatively little is known about the sorption of polar/ionizable pesticides and the non-hydrophobic interactions (compound-sediment-water). Although pesticides are regularly monitored in surface water, there are only few studies focused on simultaneous determination of pesticide residues in water and sediment samples [37\*]. In general, temporal variability of pesticide concentration in sediment samples is lower compared to water samples. Moreover, pesticide concentration in sediment is affected less by extreme rainfall and runoff events compared to water samples. More accurate results can be drawn in the monitoring studies by combining grab and passive sampling of sediment, water and biota samples.

### Water bodies

Pesticides can reach surface- and ground-water bodies from diffuse and point-source pollution sites. Diffuse contamination by pesticides is responsible for the widespread detection of low pesticide concentration, whereas point sources result in detection of high pesticide concentration. There are numerous ways for pesticides to reach and contaminate surface water bodies. Spray application or planting of pesticide dressed seeds and wind dispersal lead to the direct contamination of surface water. Dissipation of pesticides in the aqueous environment varies in terms of temperature, pH, sunlight, presence of dissolved organic matter, suspended material, algae, zooplankton, fish and microorganisms.

Photodegradation in water is a major dissipation route of pesticides from different chemical classes. Thus,

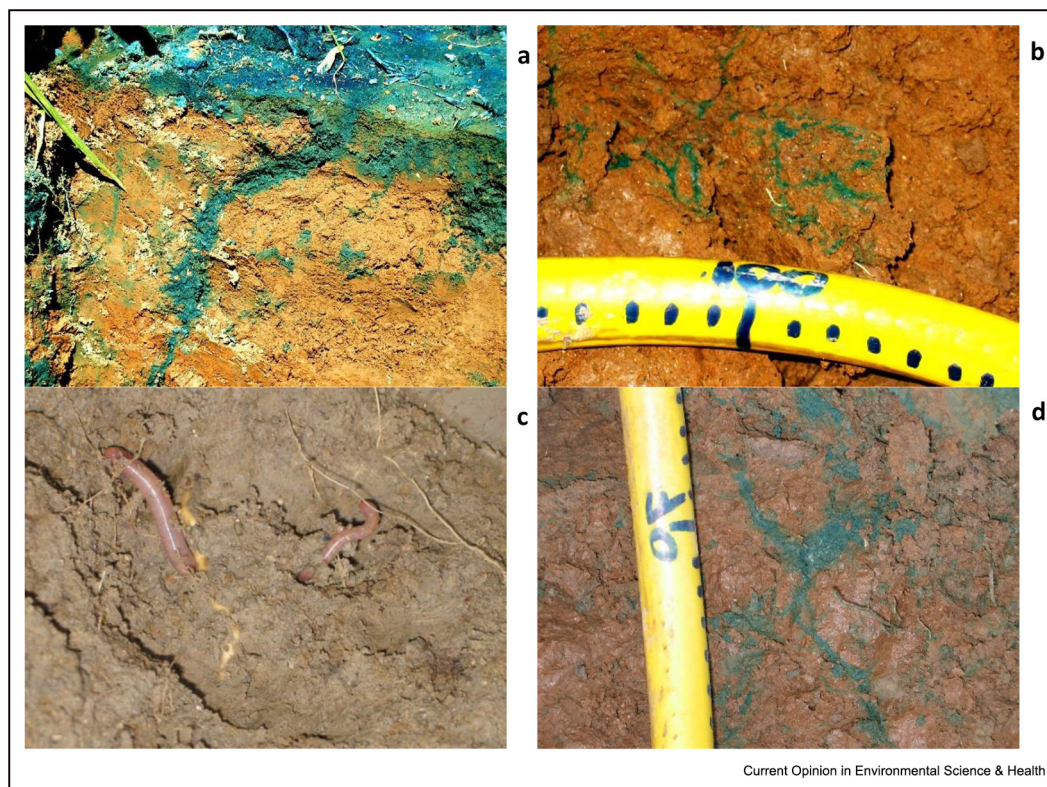
photochemical decomposition and detoxification is often used to remediate pesticide contaminated water bodies [38]. It is well documented that the degradation rates of organophosphates, neonicotinoids, phenoxyalkanoic acids, sulfonylureas, triazines and other chemical classes in water vary in terms of pH [39–41].

Pesticides are primarily transported downstream from the agricultural fields to surface waters through surface runoff and drain flow. Highly water-soluble pesticides are more likely to be moved through runoff during rainfall or irrigation. However, pesticides adsorbed in soil compartments can also be moved via suspended particulate and sediment movement during heavy rainfall events. Wauchope et al. [42] have reported that runoff varied from 5 to 15% of rainfall, while pesticide concentration in runoff is mostly affected by the frequency of precipitation and timing in relation with the application period of pesticides [43,44].

High pesticide concentrations are likely to be found close to point-source pollution sites, in unconfined shallow aquifers [44–47\*\*]. Many researchers have reported rapid pesticide movement through preferential

flow to groundwater [10,48,49]. Pesticide physico-chemical properties such as water solubility, octanol–water partition coefficient, dissociation ( $pK_a$ ) and Henry's law constants are determining factors of their leaching potential. However, in the case of preferential flow, pesticides can be rapidly transferred to groundwater irrespective of their physicochemical properties (Fig. 1). Furthermore, biodegradation, soil porosity, hydrogeology, apparent age of groundwater (water residence time) and aquifer characteristics affect the extent of groundwater contamination. Vryzas et al. [46\*] reported higher pesticide concentration in shallow groundwater from experimental boreholes compared with the respective concentrations in the adjacent deep groundwater (drinking or irrigation water wells). Mixed leaching mechanisms (“chromatographic” and preferential flow) have been reported to be involved in the contamination of adjacent aquifers with different water residence times. According to the published pesticide monitoring studies, herbicides and their transformation products are the most frequently detected pesticides in groundwater. Although most pesticide transformation products are not included in monitoring studies, they are often more abundant than their parent compounds [50–52].

Fig. 1



Preferential flow pathways: a) macroporosity (0.4–5 cm thickness) formed from the shrinkage of clay minerals, b) macroporosity (0.5–1 mm thickness) formed from the shrinkage of clay minerals and extended below the 150 cm, c) macroporosity formed from earthworm burrows, d) formed by plant roots penetration channels.



## Concluding remarks

In view of climate change, pesticide use is expected to be affected. Increase in temperature and changes in precipitation patterns (rainfastness) is expected to influence plant protection strategies and increase the use of pesticides [3]. Climate change is expected to affect the fate of pesticides in the soil-sediment-water environment. Extended dry periods followed by intense rainfall events are expected to increase the mobility of pesticides through runoff and preferential flow to surface- and groundwater bodies, respectively [53]. Moreover, increased pesticide concentrations are expected in wet deposition at the beginning of the intense and more frequently storm events [54]. Also, lower water content in surface water bodies has the potential to increase pesticide concentration during the dry season. On the contrary, higher temperatures are expected to accelerate the degradation and volatilization process of pesticides in soil-sediment-environment.

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